DEVELOPMENT OF AN OIL/WATER POLLUTION MONITOR

Frank Kossler McGrath

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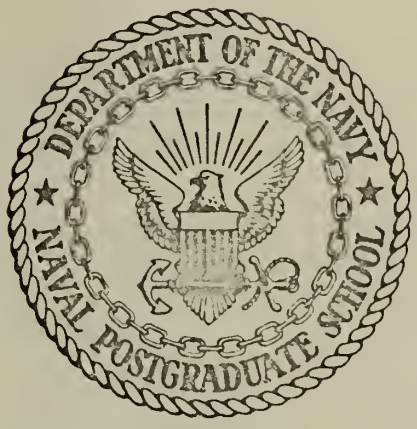

THESIS

DEVELOPMENT OF AN OIL/WATER

POLLUTION MONITOR

by

Frank Kossler McGrath

Thesis Advisor: T. Houlihan

June 1972

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Development of an Oil/Water Pollution Monitor

by

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Lieutenant, United States Navy
B.S.E., University of Michigan, 1964

Submitted in partial fulfillment of the
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June 1972

ABSTRACT

Ultrasonic wave attenuation in water with known amounts of fuel oil contaminant was measured. Attenuation was found to vary linearly with concentration of oil when the contaminant level was less than 500 ppm/volume. Investigations were conducted at a frequency of 30 Mhz in distilled water with quiescent flow conditions.

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ACKNOWLEDGEMENT

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I. INTRODUCTION

The Federal Government, by Executive Order, and under the auspices of the Environmental Protection Agency, has placed requirements on all naval and merchant vessels of this country to curb, and eventually to put an end to pollution of the sea environment by overboard discharge of contaminated water. Additionally, the Navy has issued OPNAV instructions and local directives to further insure the prevention of pollution by naval vessels. One specific area of concern is the overboard discharge of oil from bilge and ballast water.

The Naval Ships Systems Command is currently exploring the development of a reliable and ruggedized oil/water separator and monitoring system, adaptable to shipboard environment, for contaminated water with flow rates of 0-200 gallons per minute and with the effluent containing less than 25 ppm oil. The monitoring system is required to meet the following specifications:

a - reliable, rugged, and adaptable to shipboard environment

b - have a response to a suspended matter size of 50 microns

c - operate in a temperature range of 40°-120°F

d - have a one second or less response time

e - be independent of the type of petroleum used

f - have an accurate response to contaminant levels as low as 25 ppm oil in water

g - must have an electronic readout to provide both dynamic and integral evaluation

Investigations were made into the various principles and devices which could be used to develop a monitor which would meet the specifications. Operations involving changes in electromagnetic spectral

characteristics, conductivity, reflectance and absorption, optical density, membrane ionic permeability, and ultrasonic waves were studied. The choice of proceeding with development using an ultrasonic device was made for several reasons. First, the signal scattering effects found in systems featuring optical and electronic characteristic alterations were eliminated. Secondly, an ultrasonic device would have no moving parts and could be built rugged enough to easily withstand shipboard environment. Finally, the theory and the equipment necessary for the development of an ultrasonic monitor were within the state of the art, and could readily be adapted to existing shipboard type equipment. The major unknown to be determined was the accuracy of an ultrasonic device in the flow fields required by the specifications. The principal aim of this research project, therefore, was to design, to build, and to test a first generation, ultrasonic oil/water monitor.

In order that a proper base might be established for this and future research, it was further decided to test in distilled water and quiescent to low flow rates. The pollutant chosen was standard Navy distillate fuel oil, a petroleum based product which will be the fuel used on all naval vessels after 1975.

II. THEORETICAL CONSIDERATIONS

The propagation of sound in a liquid containing suspensions of small particles has been given considerable attention in the past ten to fifteen years in an effort to understand the causes of absorption of sound waves in these systems. The possible causes of absorption, due directly to the suspension, is assumed to be the sum of the following effects: (a) attenuation by scattering; (b) loss in the liquid caused by the presence of the suspended media increasing shear and volume viscosity of the liquid; and (c) losses due to intracellular processes [1].

Litovitz et al [2] conducted experiments which show that viscous flow is time dependent because the molecular units involved have a certain relaxation time, caused by the necessity for each molecule to accumulate enough energy to overcome the potentials restraining its motion. If acoustic measurements are made with a frequency, the period of which is short compared with the relaxation time, the liquid molecules are simply displaced from their equilibrium positions and no flow takes place. The liquid in these circumstances exhibits an instantaneous elasticity which is not evidenced in static or low-frequency measurements.

Capitalizing on the above observed phenomena, several researchers have investigated the propagation of ultrasonic waves in liquids containing small suspended matter. Busby and Richardson [3] studied suspensions of small glass spheres in water. They found that for low concentrations, the ultrasonic attenuation is directly proportional to concentration, showing that the interaction between particles may

be neglected. Slie and Litovitz [4] investigated the effect of an alcohol impurity on ultrasonic relaxation in liquid carbon disulfide over a frequency range from 5 - 155 Mhz. Their results showed that the relaxation frequency is a linear function of the concentration for the impurities studied, and concluded that the vibrational relaxation process was linear. Gruber and Meister [5] examined ultrasonic attenuation in water containing brine shrimp in suspension in the frequency range from 1 - 45 Mhz. They observed a linearity between attenuation and concentration in the unhatched brine shrimp solutions which indicated that interaction between particles can be neglected. They also showed that the measured attenuation passes through a maximum as a function of the frequency. Meister and St. Laurent [6] studied ultrasonic absorption and velocity measurements containing algae in suspension. The latter study is of prime importance since the parameters of the algae suspension are closely related to those used in this research project. The diameter of the suspended particles was 50 microns, and the concentration was varied. between 0 - 750 ppm. Test frequencies were varied from 15 to 27 Mhz. The conclusion of this, like the other studies mentioned, was that interaction between particles is negligible at the frequencies employed, and that ultrasonic attenuation was linear and due solely to the contaminant level.

The principle of ultrasonic wave generation featured in these studies utilizes the piezoelectric properties of crystalline quartz. The lattice structure of quartz is cubic, and extremely regular. The axis along the longest dimension of the natural crystal is the optic, or z-axis. The axis passing normal to this between any two edges

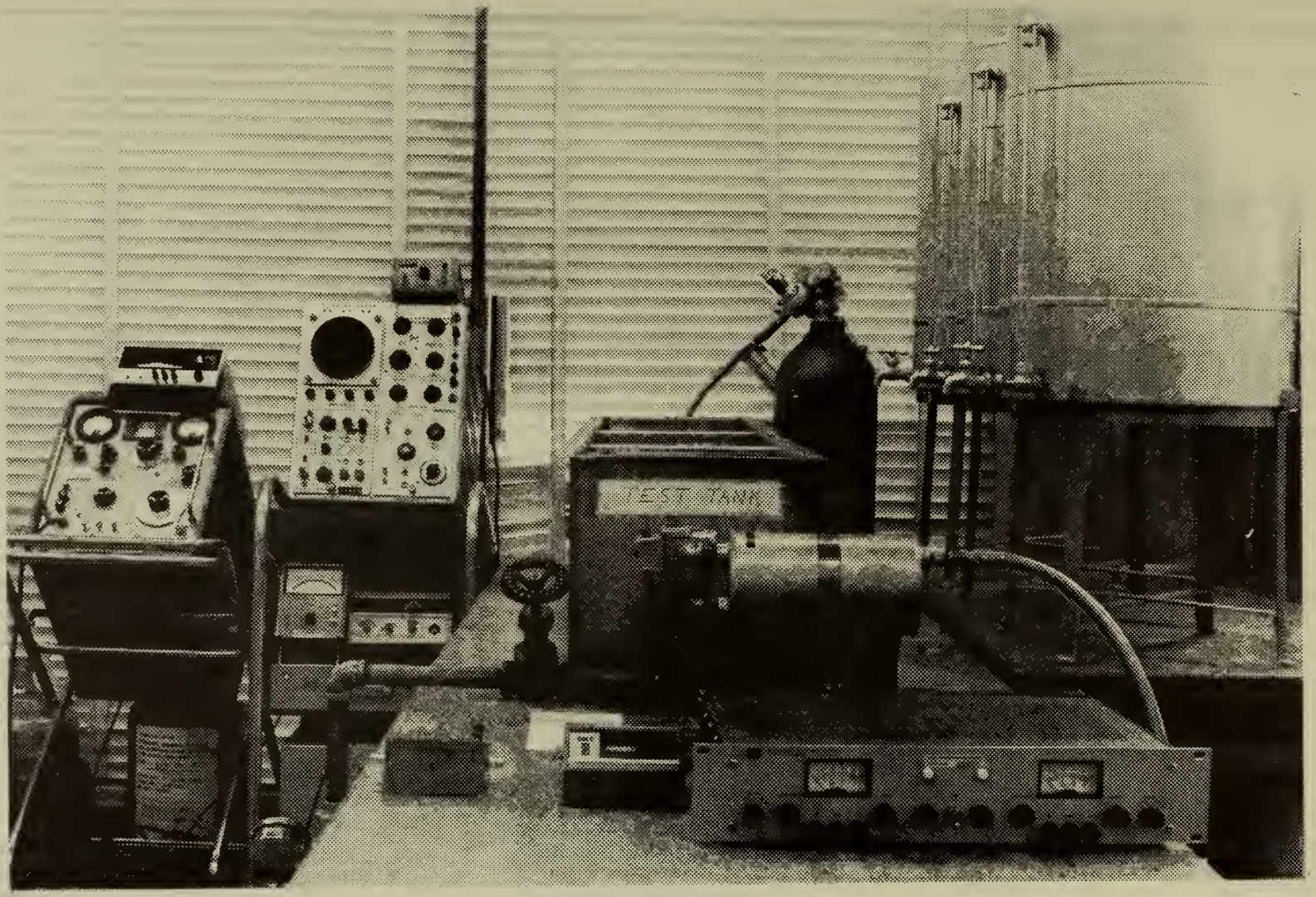
is the electric, or x-axis. The third axis normal to both is the mechanical, or y-axis. Whenever an applied stress produces a strain along the x-axis or y-axis of an X-cut crystal, the crystal becomes electrically polarized, and piezoelectric charges of opposite sign appear on the two surfaces perpendicular to the x-axis. Conversely, if these two surfaces are covered by a metal film and an electric field is applied parallel to the x-axis, the crystal will expand along the y-axis and contract along the x-axis. If an alternating electrical field is applied along the x-axis, the resulting mechanical deformations along the y-axis may be used to set up longitudinal vibrations along this axis. As the frequency of the applied electric field approaches the natural frequency of any longitudinal mode of vibration of the crystal, the amplitude of the mechanical vibration becomes quite large, approximately 0.0005" at 30 Mhz, and an ensuing pressure field is developed in a liquid in contact with the crystal. It is the attenuation of this pressure field as a function of the density of the liquid medium between a sending and a receiving ultrasonic sensor that forms the basis of the monitoring technique described herein. Ultrasonic frequencies are high - quartz crystals may be driven up to 10 - 15 Mhz in their fundamental mode, and using harmonic modes, up to frequencies as high as 500 Mhz [7].

III. EXPERIMENTAL METHOD

A. EQUIPMENT

Two quartz crystals were inserted into a cylindrical stainless steel test holder which was then placed in a tank where the concentration of the oil in the water was varied.

The crystals selected were 30 Mhz, X-cut quartz crystals. Both faces of the crystal were optically polished for overtone operation. The electroding was a gold-chromium sputter, chosen because it could better withstand the water and saltwater environment, would not break down under the applied voltage, and could be easily cleaned with a detergent wash. Overall crystal diameter was 1.000 inch, and thickness was approximately 0.0003 inch. The electroding covered one face fully and acted as a common ground attachment when placed in the holder and in contact with the water. The reverse side was electroded in only the inner 5/8" diameter. A rubber 'O' ring was placed on the non-electroded portion of this face. This effectively isolated the one side of the crystal from the test cylinder. Electrical connection, Fig. 2, was made by means of a fine brass wire wound in a coil and soldered to a BNC plug connector. This method prevented damage to the thin crystal yet made an effective contact against the crystal face. The frequency selected, 30 Mhz, was dictated by the size of the particles which had to be detected, in this case 50 microns or equivalently 0.001965". The wavelength of sound in water at 30 Mhz is 0.001965". This wavelength thus insured that relaxation effects would be detectable.



TEST EQUIPMENT

Fig. 1

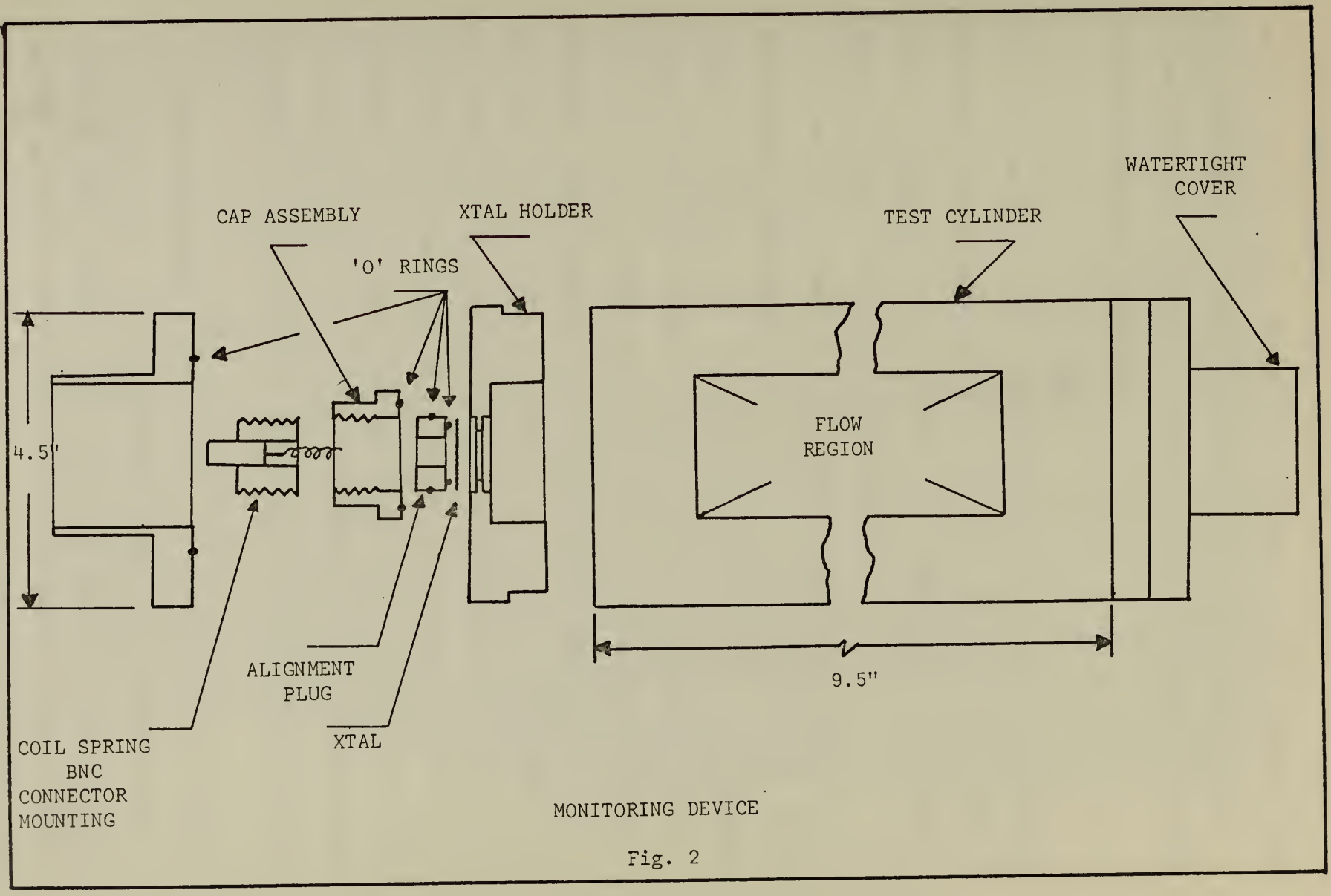

CAP ASSEMBLY
XTAL HOLDER
'O' RINGS
WATERTIGHT COVER
TEST CYLINDER
4.5"
FLOW REGION
ALIGNMENT PLUG
COIL SPRING
BNC CONNECTOR MOUNTING
XTAL
9.5"
MONITORING DEVICE

Fig. 2

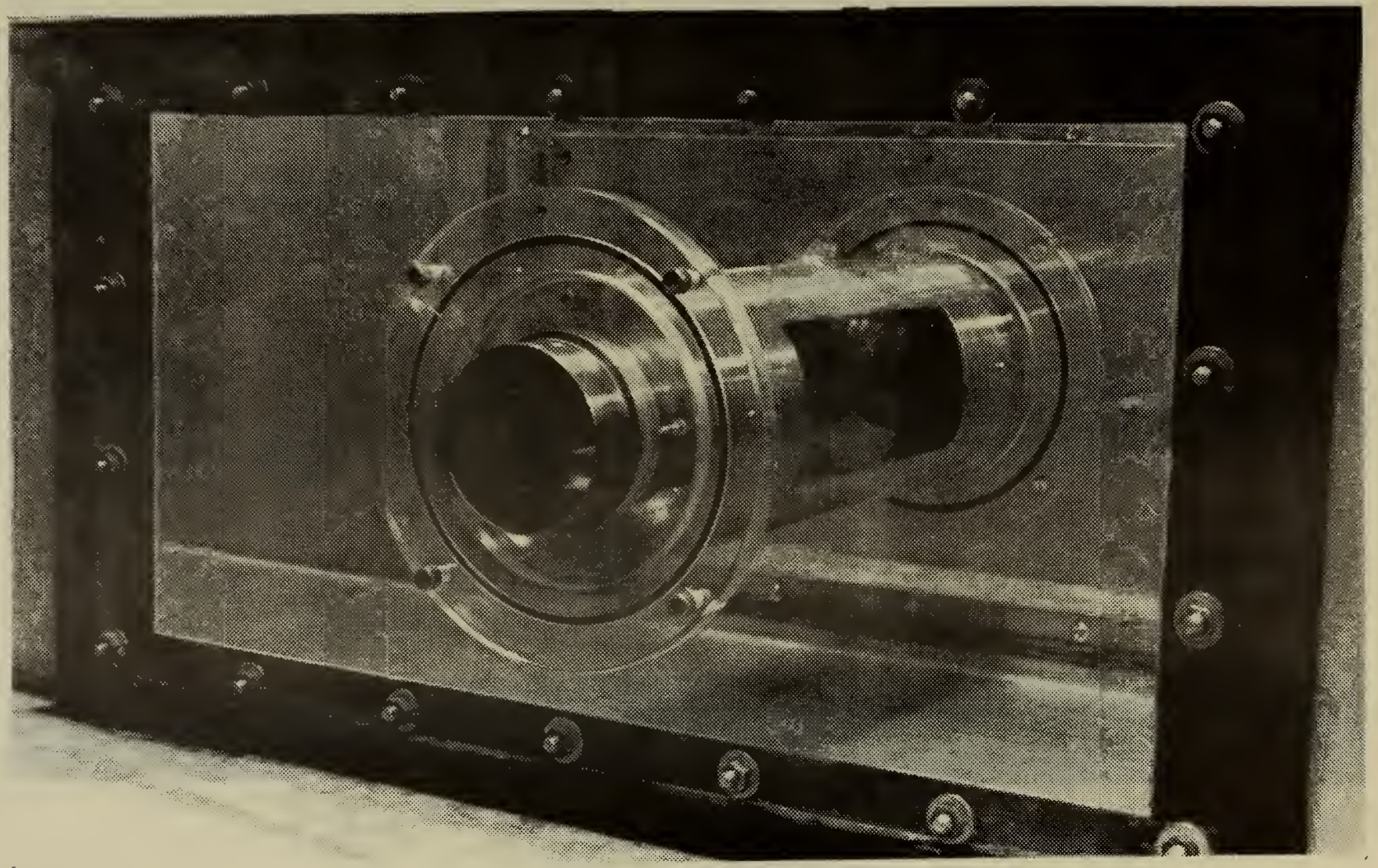
The outer diameter of the crystals was determined by taking into account the diffraction and scattering effects in the ultrasonic field of a piston source. Bass [8] recommends that the following equation be used to insure operation in the near field of the beam, thus making the diffraction loss negligible:

$$l < a^2/2\lambda$$

Here l is the total length of the ultrasonic path, λ is the ultrasonic wavelength in the liquid, and a is the radius of the circular transducer. The diameter chosen was well within these limits and commensurate with the length of the test cylinder.

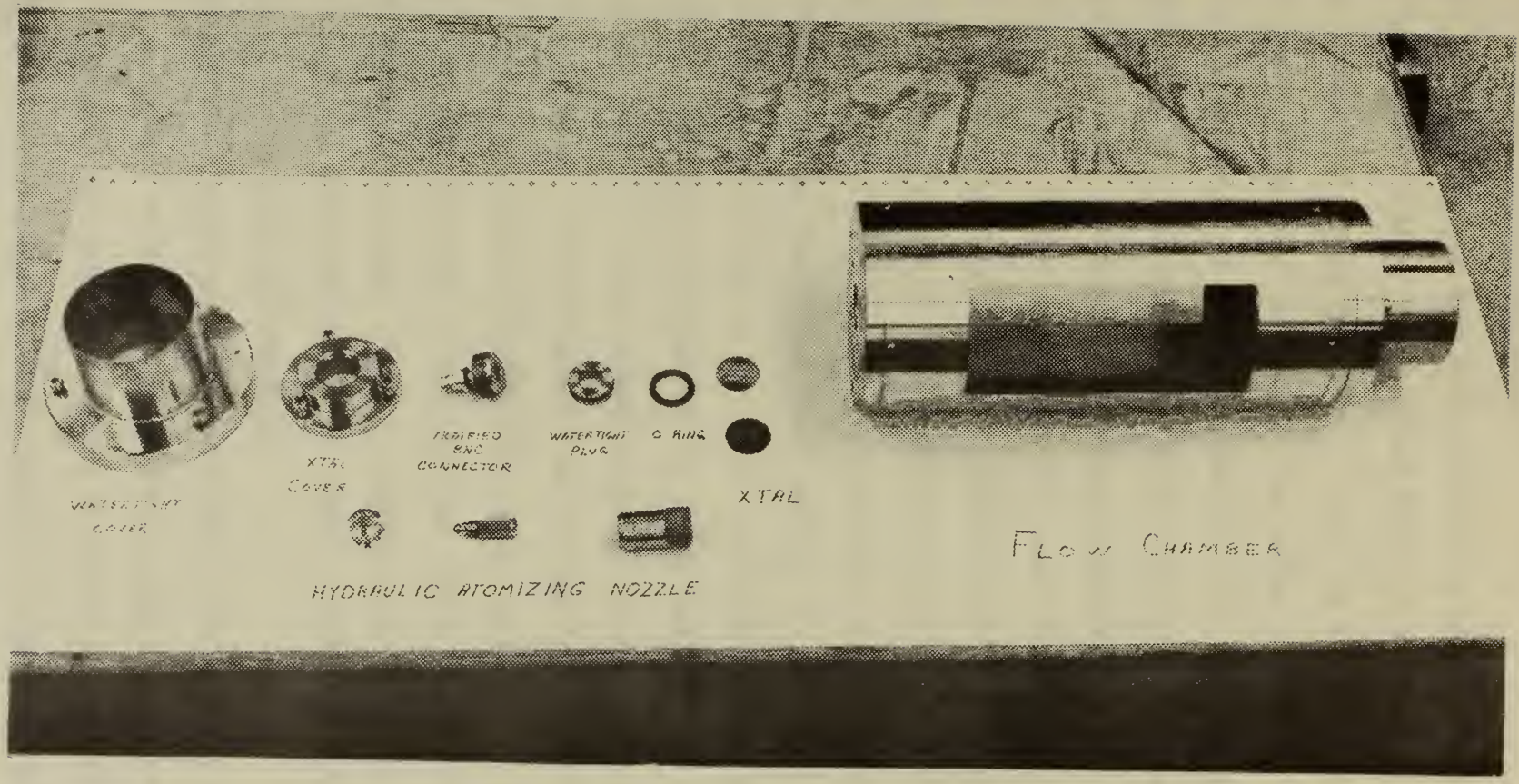
The mounting cylinder for the crystals, Figs. 2, 3, and 4 was constructed of stainless steel to avoid any loss in dimensional stability when subjected to a varying temperature field. It was desired to keep the crystals parallel to each other, thus eliminating the possibility of a phasing problem between the sending and receiving crystals. Final readings on the machined cylinder showed it to be parallel to within 0.5 mils. The length, 9.5", and the diameter, 4.5", were chosen on the basis that this would approximate, to an order of magnitude, the dimensions of a shipboard installation. A 2.5" by 6.0" horizontal cut was made in the sleeve assembly to allow flow through the ultrasonic path. Care was made to insure that the cut would not interfere with the dimensional stability, yet would insure a sufficient flow.

The end mountings, Figs. 2 and 4, were identical and constructed of stainless steel. The cap assemblies contained fitted alignment plugs and screw fixtures, within which the brass coil contact springs and BNC connectors were mounted. All mating points were made watertight by the use of 'O' ring seals. Over these assemblies were placed



MONITORING DEVICE

Fig. 3



MONITORING DEVICE

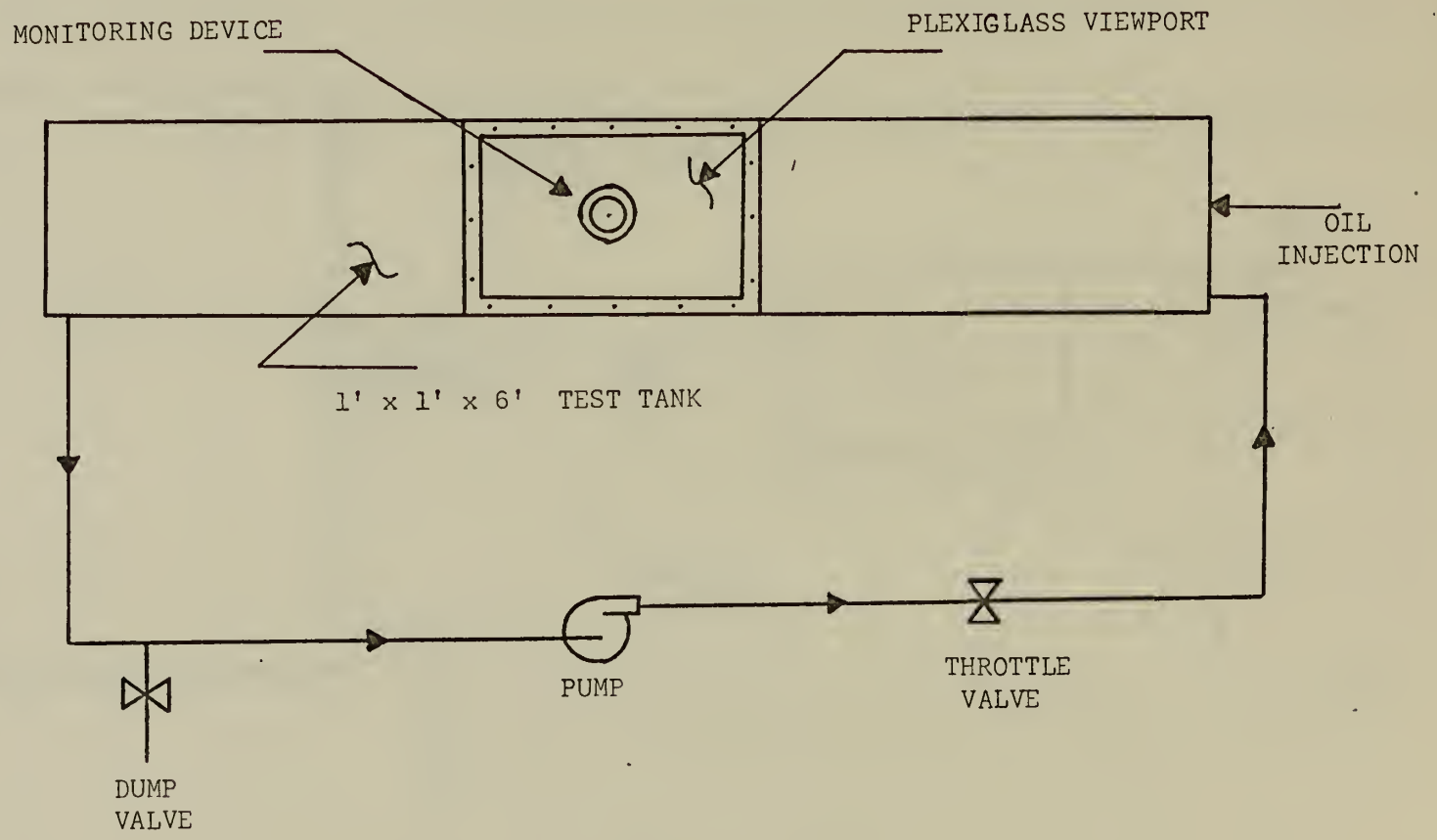
Fig. 4

the covers, which acted as supporting arms and insured watertight integrity of the complete arrangement.

The tank Fig. 5, was also constructed of stainless steel to facilitate cleaning after being filled with the oily water. The nominal dimensions of the tank were 1' by 1' by 6' and could hold approximately 45 gallons of water. The center portion of the side walls was constructed of plexiglass and held the test section. All connections to the tank were sealed with plastic putty to avoid any collection of the contaminant. A recirculating system was used to facilitate mixing of the contaminant and insure homogeneous mixing action. A small capacity pump was installed with a throttling valve, allowing measurements to be made under turbulent flow conditions.

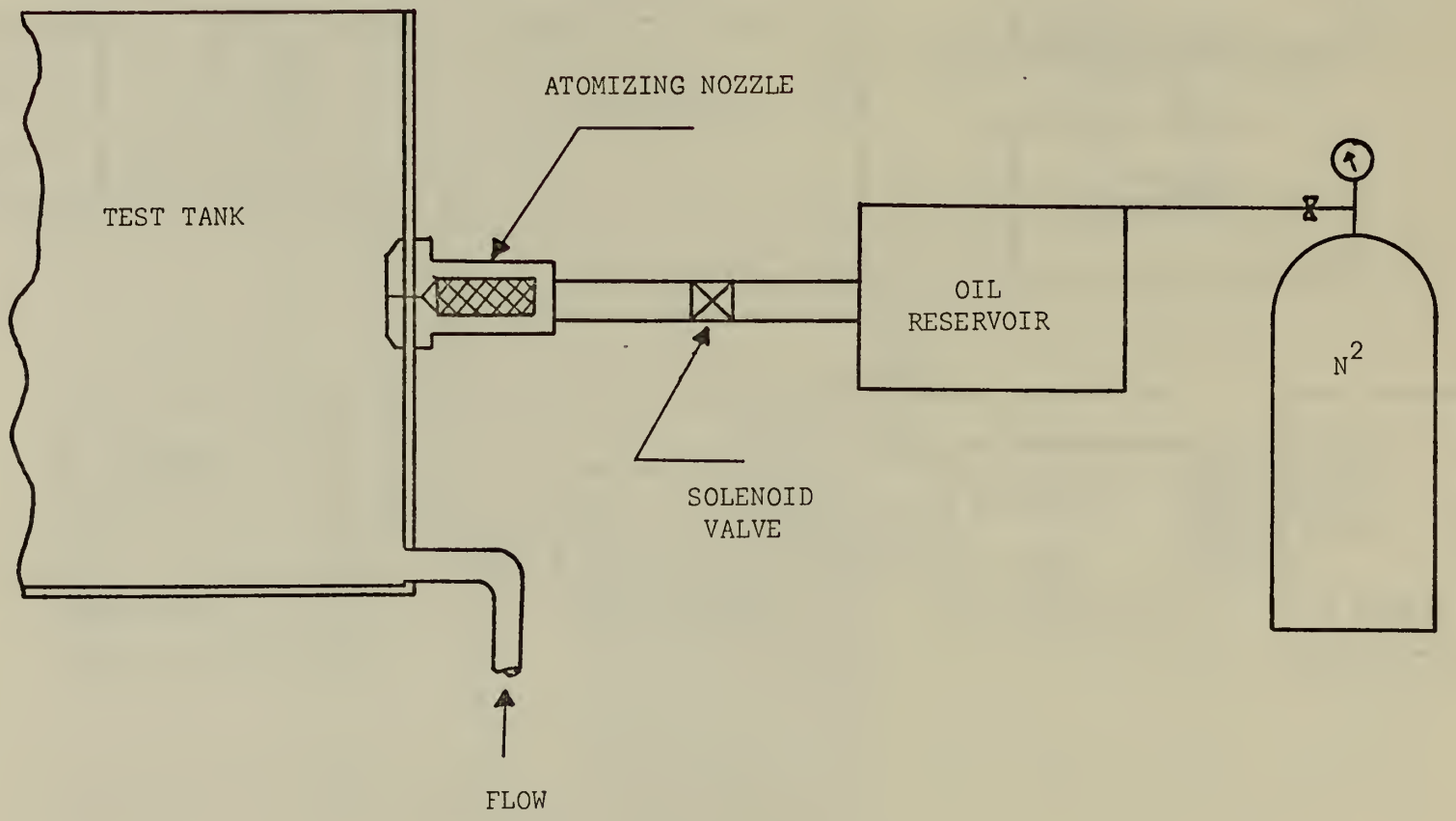
The injection system for the pollutant oil, Fig. 6, consisted of a hydraulic atomizing nozzle which sprayed the oil into the water at the midpoint of one end of the tank. The mean size of the spray particles, according to manufacturer's specifications, was 50 microns. The oil was stored in a half-gallon reservoir charged to a pressure of 80 psi by means of a nitrogen bottle and was then admitted to the nozzle through a solenoid valve. Knowing the rate of flow from the nozzle at 80 psi and using a stopwatch for timing the solenoid valve, a known amount of pollutant could be added to the 45 gallon water tank. This system gave excellent results in that a thoroughly homogeneous mixture of oil in water was obtained.

Two different types of signal generators were used for electrical input. A standard shipboard type AN/URM-25 signal generator was used first. However, time precluded making the necessary modifications to insure the constant signal voltage required. A Hewlett-Packard 608-C signal generator was subsequently introduced to provide the input signal.



TEST TANK

Fig. 5



OIL INJECTION SYSTEM

Fig. 6

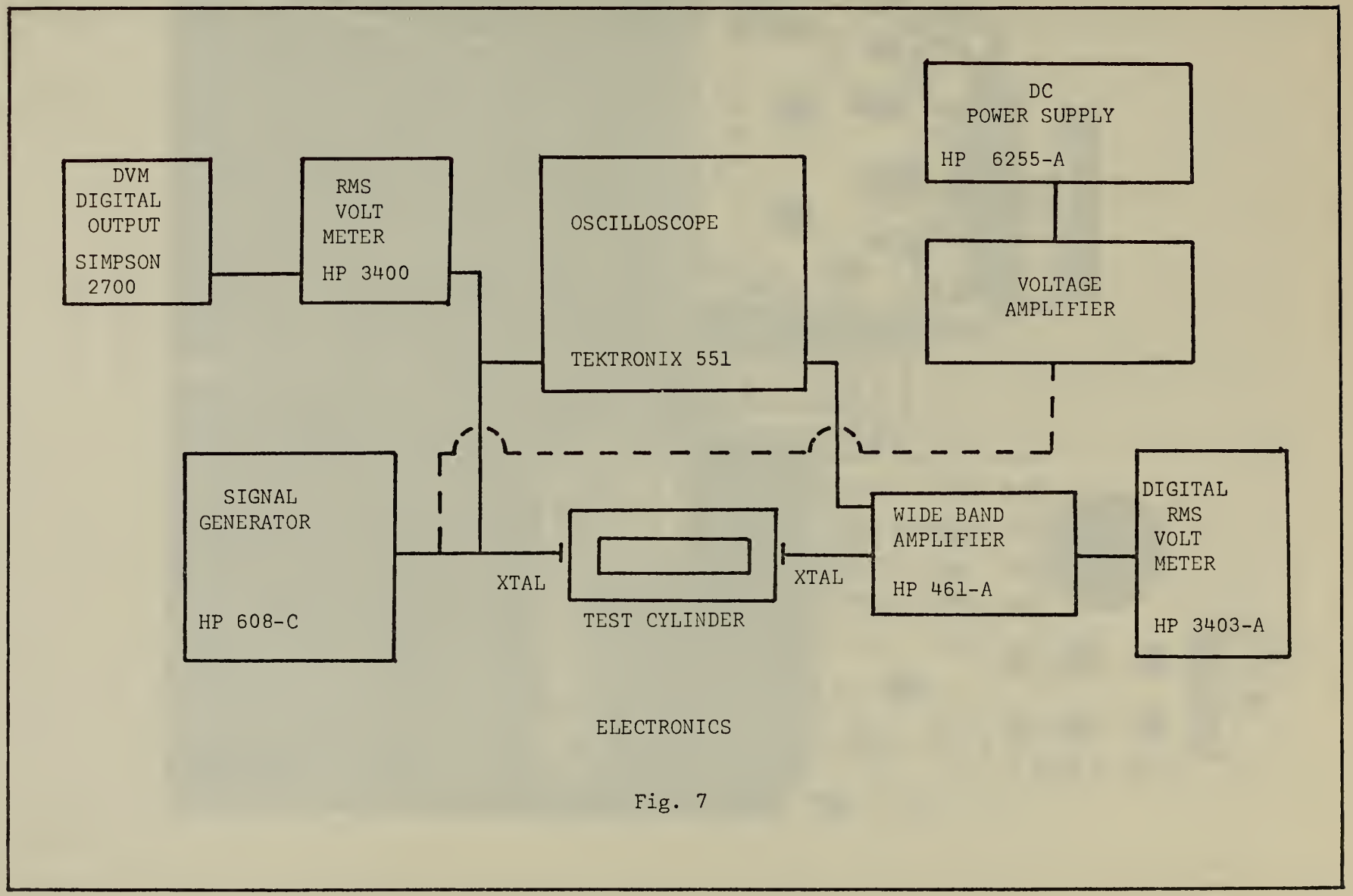
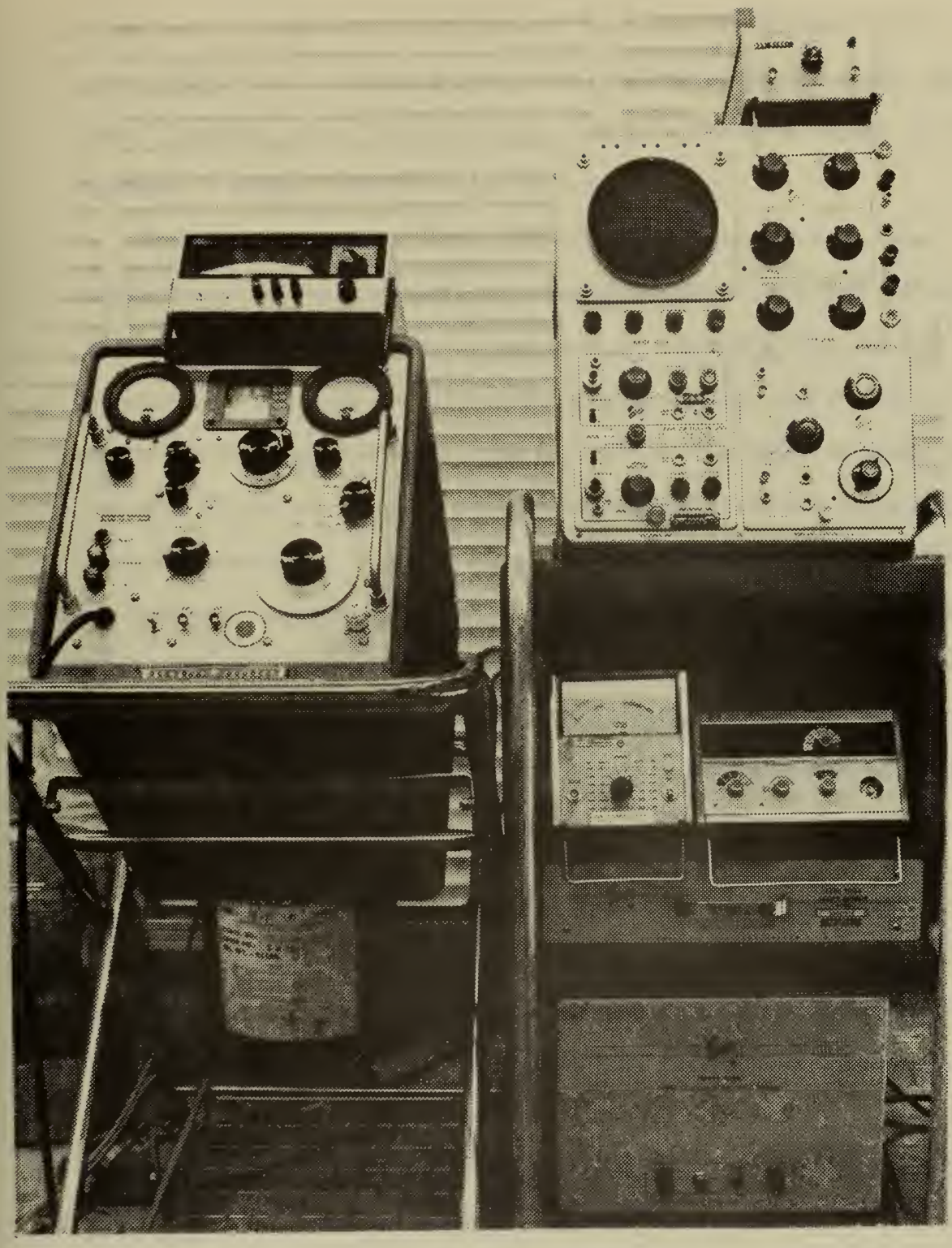

DC
POWER SUPPLY
HP 6255-A
DVM
DIGITAL
OUTPUT
SIMPSON
2700
RMS
VOLT
METER
HP 3400
OSCILLOSCOPE
TEKTRONIX 551
VOLTAGE
AMPLIFIER
SIGNAL
GENERATOR
HP 608-C
XTAL
TEST CYLINDER
XTAL
WIDE BAND
AMPLIFIER
HP 461-A
DIGITAL
RMS
VOLT
METER
HP 3403-A
ELECTRONICS

Fig. 7



ELECTRONICS

Fig. 8

In an attempt to increase the input signal voltage, a two transistor, tuned coil voltage amplifier, powered by a Hewlett-Packard 6255-A DC power supply was introduced into the circuitry after the signal generator. However, line losses and the lack of a means to adjust the coil rendered a minimal amplification effect.

The input voltage was monitored on a Tektronix 551 duel beam oscilloscope and concurrently on a Hewlett-Packard 3400 RMS voltmeter. The DC output of the RMS meter was read on a Simpson 2700 DVM for closer resolution. Although the ultrasonic signal was outside the 10 Mhz bandwidth of the input RMS meter, the roll-off of the meter response curve was mild enough to insure a sufficient reading at 30 Mhz to effect accurate monitoring of input signal levels. Readings from the receiving crystal were amplified through a Hewlett-Packard 461-A wide band amplifier, set on a 40 db gain. The output voltage level was read on a Hewlett-Packard 3403-A RMS meter with a digital output in the millivolt range and concurrently on the oscilloscope using an H-type plug-in.

B. PROCEDURE

Initial flow field measurements, to insure continued adequate mixing, were made by use of a hot film anemometer. Water flow on both sides of the cylinder at the midpoints and side of the flow cut was monitored, and a thoroughly perturbed flow pattern was determined to exist under all flow conditions.

An ultrasonic field was established between the two crystals with pure distilled water as the liquid medium, thus allowing base readings to be established. Oil in increments of 25 ppm, was injected into the water and circulated for approximately five minutes. The homogeneous mixture was then allowed to come to rest. Output voltage level readings

were then recorded at each level of pollutant. Readings of the turbulent flow voltage level at each increment of pollutant were also attempted. Input voltage was held constant to within $\pm$ 0.5 millivolts during this process. The maximum level of pollutant was 500 ppm.

After each pollution run the entire system was cleaned and flushed using common household detergent, followed by a thorough rinsing and a distilled water washdown.

IV. RESULTS

Five runs were made with distilled water as the base fluid. The first run was performed for an operational checkout of the equipment and produced no results except those of a gross nature. At this time, oscilloscope readings alone of both input and output signal levels were recorded. The initial meter-recorded results, as shown in Fig. 9, were not encouraging; although, again from a gross standpoint, the attenuation did increase with pollutant. A succeeding run was made under identical conditions. However, at this time the input voltage was continuously monitored and controlled to within a $\pm$ 0.5 millivolts level on the Simpson DVM monitor. The attenuation results were linear, as can be seen in Fig. 10. Successive runs were made using a higher and lower input voltage, again closely controlled. Results, Figs. 10 and 11, showed the same linear attenuation, but with a steeper slope for the higher input voltage and lesser slope for the lower input voltage.

Several runs were made with ordinary tap water, both unfiltered and filtered for solid particulate matter. The output voltage fluctuated over a 40 - 50 millivolt range without any contaminant and showed negligible variation in output range when small amounts of contaminant were added. Even though a voltage amplifier was added to the system input, wide fluctuations in output were still observed.

It was observed that the output voltage was affected by the intensity of the turbulence in the flow. Measurements were not recorded during these flow situations due to the lack of the necessary equipment to filter and to correlate the output signal.

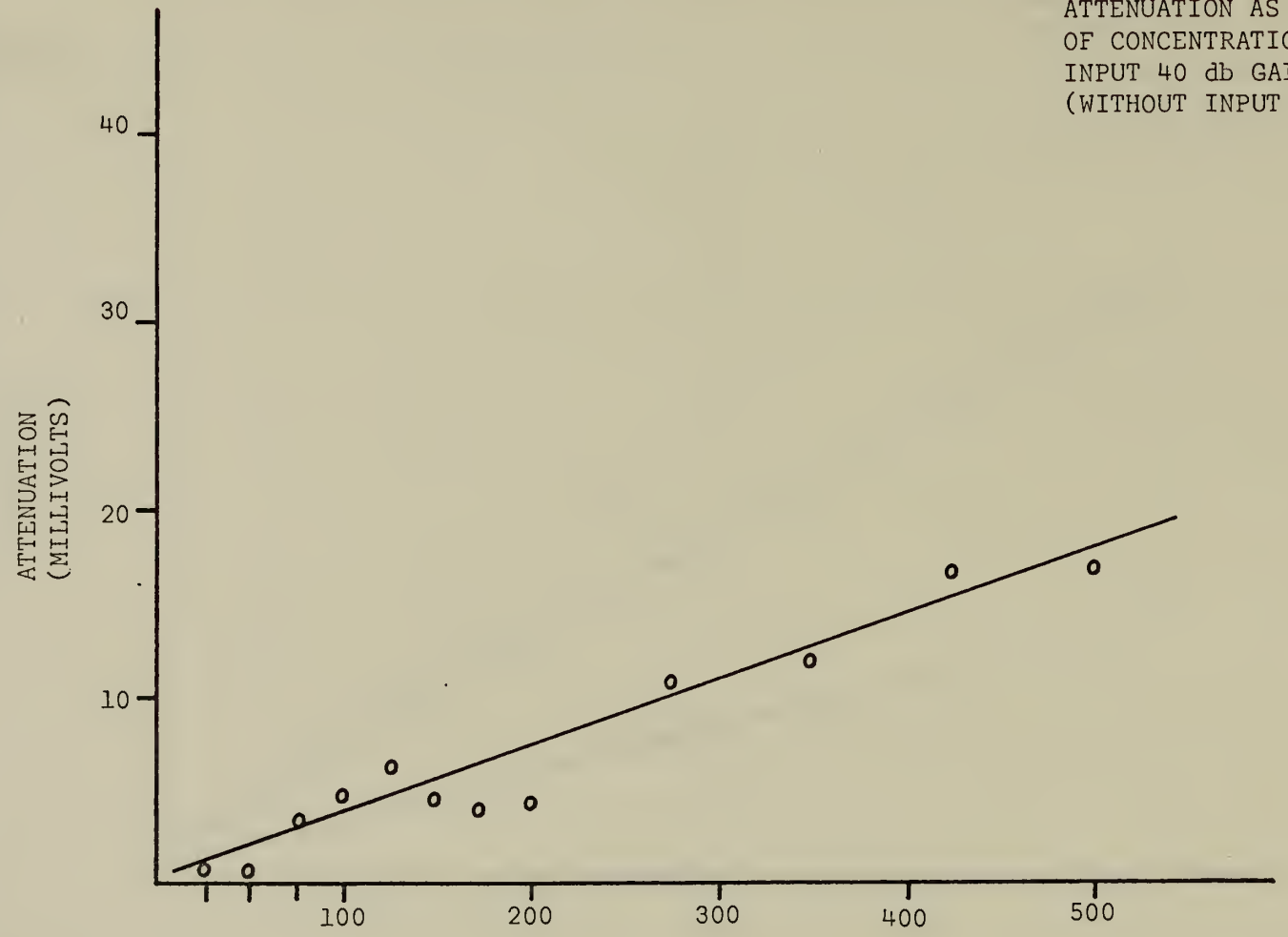
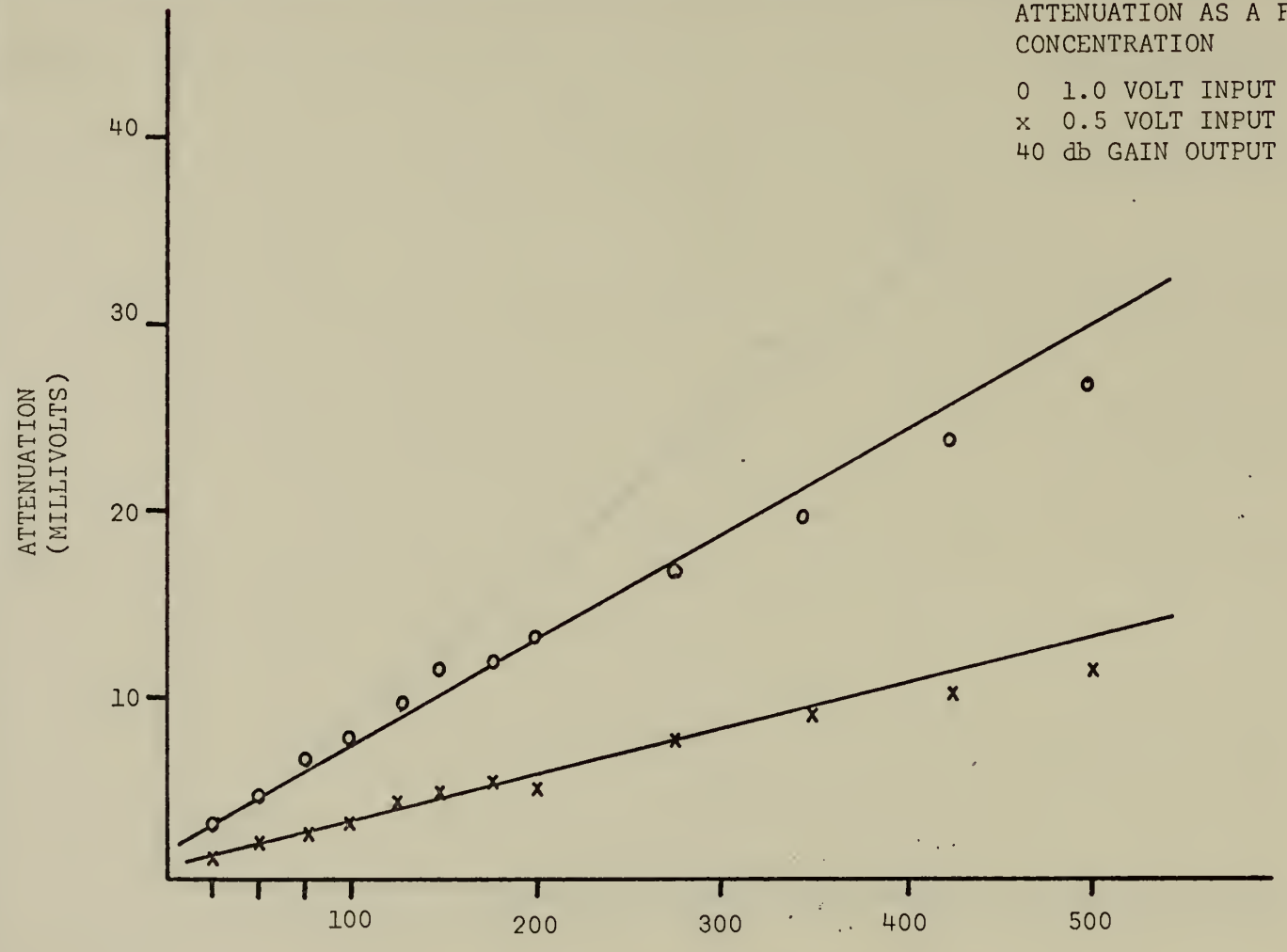

ATTENUATION AS A FUNCTION
OF CONCENTRATION 1.0 VOLT
INPUT 40 db GAIN OUTPUT
(WITHOUT INPUT MONITORING)
ATTENUATION
(MILLIVOLTS)
40
30
20
10
100
200
300
400
500
CONCENTRATION (PPM)

Fig. 9


ATTENUATION AS A FUNCTION OF CONCENTRATION
0 1.0 VOLT INPUT
x 0.5 VOLT INPUT
40 db GAIN OUTPUT
ATTENUATION (MILLIVOLTS)
40
30
20
10
100
200
300
400
500
CONCENTRATION (PPM)
Fig. 10

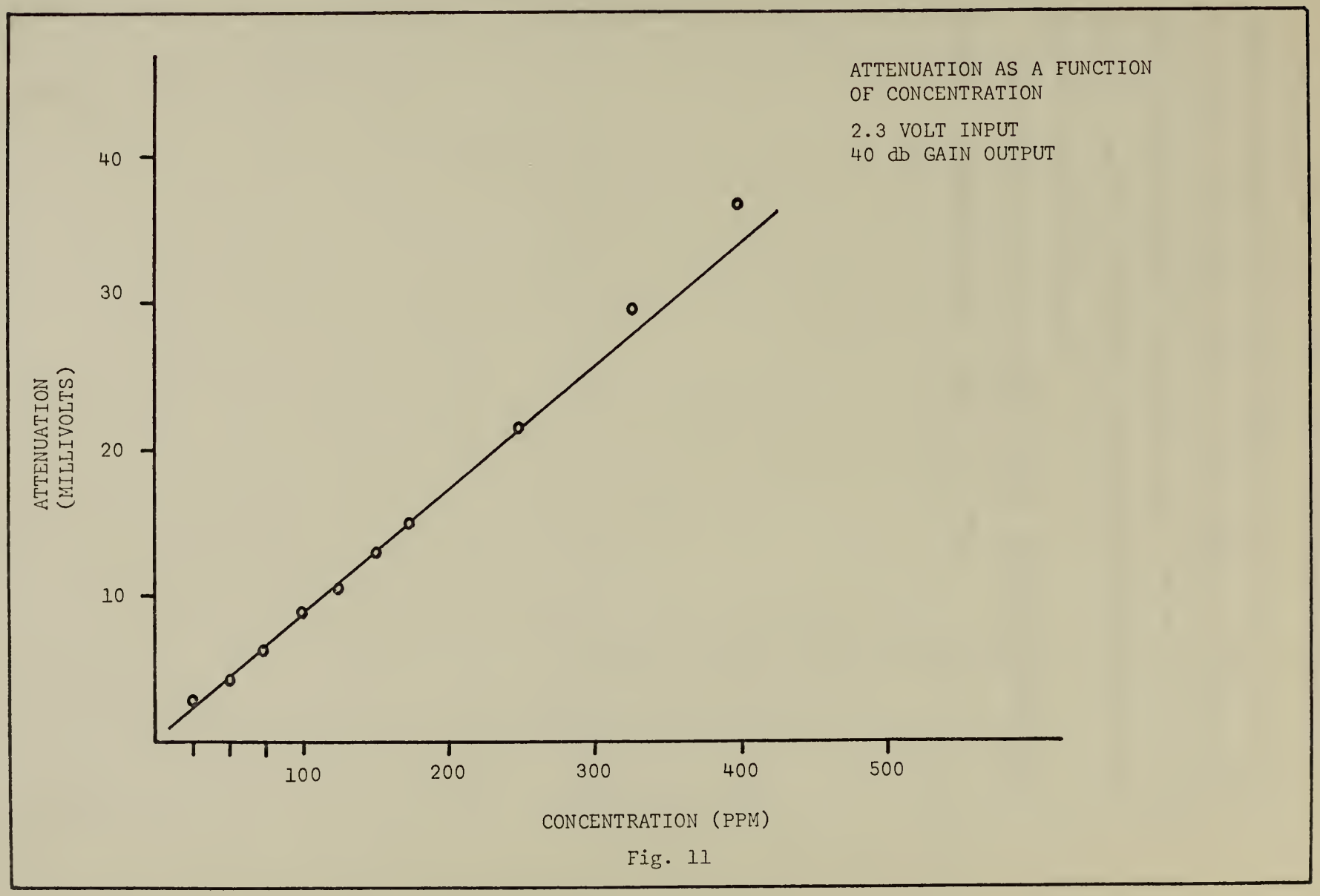

ATTENUATION AS A FUNCTION
OF CONCENTRATION
2.3 VOLT INPUT
40 db GAIN OUTPUT
ATTENUATION
(MILLIVOLTS)
40
30
20
10
100
200
300
400
500
CONCENTRATION (PPM)

Fig. 11

Results of the initial flow field study with the hot film anemometer showed that extreme mixing and reversing of flow existed in the tank. This had no effect on data readout as quiescent flow conditions were used for the recorded data. However, the initially agitated flow field did ensure a homogeneous oil/water environment for the ultrasonic wave path.

Bench testing of the unloaded crystals showed that they would fracture at approximately 60 volts at 30 Mhz.

V. CONCLUSIONS

The primary goal of this project was achieved in that the feasibility of an ultrasonic pollution monitoring device was proven. Oil molecules, in small concentrations, do have a linear attenuation effect on an ultrasonic path. The sensitivity of this monitor and the associated electronic equipment meets the required specifications, in distilled water, as to particle size, response time, and data output. The temperature range will not present a problem, as the stainless steel test section will not vary in dimensions over the 40° - 120°F range. The effect of the turbulent flow can be overcome with proper filtering of the output signal as the frequency of the turbulence is much lower than that of the ultrasonic signal. The requirement of response, independent of the oil in suspension, will have to be investigated. Different oils have different miscibility levels in water, and although a linear response is anticipated, the sensitivity of the output reading will vary.

The area of greatest concern is the lack of conclusive response in tap water. Gross additions of 75 - 100 ppm did effect attenuation, but the data points were too scattered to justify any conclusions. The mineral, ion, and particulate content of the tap water seem to have an effect greater than that of the oil contaminant.

Input voltage levels do have an effect on the output sensitivity. The higher the voltage the greater the sensitivity, and conversely for the lower voltage. The results also show a non-linear effect above 300 ppm. This deviation is not great, but it does seem to indicate some molecular interaction in the dissipation of energy. This was not the case in the lower contaminant ranges, which are of the greatest concern.

It should be noted that the output readings were in millivolts, after being amplified through a 40 db gain, and that the change recorded for a 25 ppm increase in the pollutant was on the order of 2 - 4 millivolts. Thus, input voltage fluctuations, even without amplification, will have a serious detrimental effect on the stability of the attenuated signal.

VI. RECOMMENDATIONS

It is recognized that the results of this thesis represent only first generation efforts in developing an actual shipboard device. There are, however, many avenues open for further development of this ultrasonic monitor. It would appear the greatest effort should be in extending operation to a saltwater and freshwater environment. The effect of turbulence is not that difficult a problem to overcome. Investigations of ultrasonic signals in turbulent flows, both in air [9] and water [10] have been conducted with some very satisfying results.

Geometrical parameters of the monitor can be varied. The length of the ultrasonic path; the entrained flow field; and the size, shape, and material of the crystals can be changed. The quartz crystals used were cut for overtone operations at a maximum of 30 Mhz. While this was sufficient to produce the desired relaxation phenomena, it was restrictive in the sense that higher frequency ranges which would insure higher sensitivity were not investigated. The possibility of using an array of crystals, at various frequencies, to filter out different contaminant levels found in ambient water should definitely be an area of further investigation.

Voltage levels have a great effect on the sensitivity of the output. This area should also be investigated in more depth.

Finally, the promise of this device opens the door to a solution of one of man's most pressing problems - pollution - and it is strongly recommended that this work be continued, lest this door be prematurely closed.

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13. ABSTRACT

Ultrasonic wave attenuation in water with known amounts of fuel oil contaminant was measured. Attenuation was found to vary linearly with concentration of oil when the contaminant level was less than 500 ppm/volume. Investigations were conducted at a frequency of 30 Mhz in distilled water with quiescent flow conditions.

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pollution monitor						

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